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(54) Title: BALLISTIC COMPOSITE (57) Abstract A rigid ballistic composite is disclosed having a plurality of fabric layers embedded in a matrix resin wherein the fabric of the layers is made from yarn of p-aramid having a combination of specially high tenacity and elongation to break.		

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1
Title

Ballistic Composite

Background of the Invention

Field of the Invention

5 This invention relates to composite ballistic structures with a matrix resin and a plurality of fabric layers embedded therein. The fabric layers are made from p-aramid yarns which exhibit a combination of especially high tenacity and elongation to break.

10 Description of the Prior Art

 European Patent Publication No. 323,541, published July 12, 1989 discloses a rigid composite useful in ballistics applications wherein para-aramid yarns coated by a solid adhesion modifier are embedded in a
15 resin matrix of polyester, phenolic, or polyamide. That publication contains no appreciation of the importance of the combination of high yarn tenacity coupled with high elongation to break for improved ballistics performance.

 Research Disclosure No. 30527, published
20 September, 1989, discloses the use of certain para-aramid yarns in composites useful for helmet construction. The Research Disclosure contains no appreciation of the importance of the combination of high yarn tenacity coupled with high elongation to break for improved
25 ballistics performance.

 United States Patent No. 4,850,050 issued July 25, 1989 on the application of Droste et al., discloses body armor made from p-aramid yarns comprising filaments of low individual linear density. The ballistic
30 performance of the structure of that invention was reported to represent a 5% improvement over the comparison fabric of the prior art.

 United States Patent No. 4,859,393 issued August 22, 1989 on the application of Yang and Chiou, discloses a
35 process for making p-aramid yarns said to have a high elongation at break.

 United States Patents No. 3,869,429 and 4,560,743, issued March 4, 1975 and December 24, 1985, respectively, each disclose para-aramid fibers of high

quality. There is no disclosure² of any specially recognized utility for fabrics from these fibers in ballistic protection.

Summary of the Invention

5 The present invention provides a rigid composite comprising a resin matrix and a plurality of fabric layers made from p-aramid yarns exhibiting an elongation to break of greater than 4.0%, a modulus of less than 600 gpd, and a tenacity of greater than 23 gpd. The composite of the
10 invention is, generally, 50 to 90, weight, percent yarn; and the yarn is preferably a para-aramid. The matrix resin is a polyester, a phenolic, a polyamide, or a polyolefin. It is preferred that the yarn filaments be coated by a solid adhesion modifier and the adhesion
15 modifier is, generally, a perfluoroalkylether ester or paraffin wax.

 The composite exhibits excellent ballistics performance; and it has been found especially suited for use in helmets.

20 Detailed Description of the Invention

 Ballistic structures have long been made using p-aramid fibers. Fibers of p-aramids are extremely strong on a weight basis and provide good ballistic protection with a relatively high degree of flexibility.

25 There has been great effort expended in developing composite structures with improved ballistic performance because even small improvements save the lives of users of ballistic materials. Each improvement is hard-won and highly significant. The present invention
30 represents an improvement in ballistic performance, measured by V_{50} , of at least 5% for small projectiles.

 Of all the fiber properties usually measured, it has been found that the combination of tenacity and elongation to break is one of the most important
35 parameters for determining ballistic performance of p-aramid fibers. These two properties determine yarn toughness, that is, the ability to absorb energy; and yarn toughness appears to show a strong correlation with ballistic performance. While p-aramid fibers exhibit

3
remarkable ballistic performance even at moderate tenacity of 23 grams per denier and elongation at break of 3.5%, the ballistic performance is rather dramatically improved with any increase in toughness.

5 Because the tensile stress-strain curves for p-aramid fibers are nearly linear, there is a relatively simple relationship among tenacity, modulus, and elongation, that is, no single one of these properties is independently variable. It has been found that increasing
10 tenacity and modulus at constant elongation may produce modest improvements in ballistic performance but not to the extent found in practice of the present invention. On the other hand, increasing modulus at constant tenacity reduces elongation and lowers ballistic performance. When
15 both tenacity and elongation are increased at constant or reduced modulus, however, the most substantial increases in ballistic performance are realized.

By "p-aramid" is meant para-oriented, wholly aromatic polycarbonamide polymers and copolymers
20 consisting essentially of recurring units of the formulae
 $-(\text{NH}-\text{AR}_1-\text{NH}-\text{CO}-\text{AR}_2-\text{CO})-$ and
 $-(\text{NH}-\text{AR}_3-\text{CO})-$

wherein AR_1 , AR_2 , and AR_3 , which may be the same or different, represent divalent, para-oriented aromatic
25 groups. By "para-oriented" is meant that the chain extending bonds from aromatic groups are either coaxial or parallel and oppositely directed, for example, substituted or unsubstituted aromatic groups including 1,4-phenylene, 4,4'-biphenylene, 2,6-naphthylene, and 1,5-naphthylene.
30 Substituents on the aromatic groups other than those which are part of the chain extending moieties should be nonreactive and must not adversely affect the characteristics of the polymer for use in the practice of this invention. Examples of suitable substituents are
35 chloro, lower alkyl and methoxy groups. The term para-aramid is also intended to encompass para-aramid copolymers of two or more para-oriented comonomers including minor amounts of comonomers where the acid and amine functions coexist on the same aromatic species, for

example, copolymers produced from reactants such as 4-aminobenzoyl chloride hydrochloride, 6-amino-2-naphthoyl chloride hydrochloride, and the like. In addition, p-aramid is intended to encompass copolymers containing
5 minor amounts of comonomers containing aromatic groups which are not para-oriented, such as, for example, m-phenylene, 3,4'-biphenylene ether, and 4,4'-biphenylene ether.

The preferred para-aramid for practice of this
10 invention is poly(p-phenylene terephthalamide) (PPD-T); and by "poly(p-phenylene terephthalamide)" is meant the homopolymer resulting from mole-for-mole polymerization of p-phenylene diamine and terephthaloyl chloride and, also, copolymers resulting from incorporation of small amounts
15 of other aromatic diamine with the p-phenylene diamine and of small amounts of other aromatic diacid chloride with the terephthaloyl chloride. As a general rule, other aromatic diamines and other aromatic diacid chlorides can be used in amounts up to as much as about 10 mole percent
20 of the p-phenylene diamine or the terephthaloyl chloride, or perhaps slightly higher, provided only that the other diamines and diacid chlorides have no reactive groups which interfere with the polymerization reaction.

The composite of this invention requires fabrics
25 made from para-aramid yarns which exhibit an elongation to break of at least 4.0%, a tenacity of at least 23 grams per denier, and a modulus of less than 600 grams per denier. It has been determined that the surprising improvement in ballistic performance results from the use
30 of fibers having a combination of high elongation to break and high tenacity.

Ballistic composites of this invention are manufactured with yarns which have been made into fabrics; and the fabrics are impregnated by a matrix resin and
35 cured or consolidated after being formed into panels or helmets or other composite structures for ballistics protection. The kind of fabric to which the yarn is applied is not important to realize the benefit of the invention. That is, for any fabric pattern, ballistic

performance of composites obtained using the yarn of this invention will be improved over that obtained using a similar yarn having a lower toughness due to lower tenacity or lower elongation to break.

5 Ballistic composites using p-aramid fabrics are usually made with several layers of fabric laid or sewn together to yield a laminated structure. The layers can be impregnated with matrix resin individually before assembly of the laminated structure or the structure can
10 be impregnated after assembly. The laminated structure can include additional layers of other materials such as decorative or moisture resistant covering fabrics or other shock absorbing materials or ceramics or metals or other fabrics made from other fibers; and additional layers can
15 be included as covering for the composite. The form of the composite structure, and whether or not it includes additional layers of other materials, is not important to realization of the improved ballistic performance of this invention. It has been discovered that the effectiveness
20 of any composite ballistic structure will be improved by utilization of yarn having the combination of relatively higher tenacity and elongation to break instead of similar yarn having relatively lower tenacity and/or elongation to break.

25 The matrix resin component of the composite of this invention is a polyester, phenolic, polyamide, or polyolefin resin; and can be thermosetting or thermoplastic. Such materials are well known in the art and, in the cured or consolidated state, provide strong
30 rigid structures. Among suitable polyester resins, there may be mentioned vinyl ester resins, isophthalic- and orthophthalic-polyester resins. Vinyl ester resins are the reaction products of an epoxy resin and an unsaturated aliphatic acid such as methacrylic or acrylic acid.
35 Typical epoxy resins used to make resins in this vinyl ester class are of the diglycidyl ether/bisphenol-A type but may, also, be such components as epoxy novolac or halogenated epoxy.

Orthophthalic polyesters are the reaction product of a glycol, an unsaturated aliphatic dibasic acid or its anhydride, and a saturated ortho aromatic acid or its anhydride. Isophthalic polyesters utilize isophthalic acid as the saturated acid component. The glycol is usually propylene glycol but may be other glycols such as ethylene glycol, diethylene glycol, dipropylene glycol, or a combination, and the like. The unsaturated dibasic acid or anhydride is usually maleic acid, fumaric acid, or maleic anhydride; but may be other similar acids or anhydrides. The ortho aromatic acid or anhydride is usually orthophthalic acid or phthalic anhydride while isophthalic acid is the usual saturated acid in isophthalic resins. Of course, other saturated ortho or iso aromatic acids may be used, as well as modified acids such as those halogenated with chlorine. Vinyl ester resins and orthophthalic and isophthalic polyester resins are generally cured by reaction with a monomer such as styrene or a substituted styrene such as vinyl toluene or alpha-methyl styrene; but other monomers may also be used such as methyl methacrylate, methyl acrylate, diallyl phthalate, triallyl cyanurate, and the like.

Phenolic resins can be of the resole type or the novolac type. Generally, the resole type is used in this invention. The phenolic resins are generally made from the reaction between a phenol and an aldehyde. Formaldehyde is usually used but, as is well-known, other aldehydes could also be suitable. Phenol is usually used but other suitable phenols include resorcinol and ring-substituted phenols such as ortho-, meta-, or para-cresol, bisphenol A, p-t-butyl phenol, p-phenylphenol, and the like.

Polyamide resins and other thermoplastic resins may, also, be used as the matrix component of the composite of this invention. Such resins must be melt-processable, preferably at below 350° C. Within the polyamide family, many types of such resins are useful, including aliphatic, cycloaliphatic and aliphatic-aromatic polyamides. These include 6,6 nylon; 6 nylon; 6,10 nylon;

6,12 nylon; polyamide from 4,4'-bis(aminocyclohexyl) methane and dodecanedioic acid; poly(hexamethylene terephthalamide); poly(hexamethylene isophthalamide); and the like. Copolymers of the above polyamides are also
5 useful.

Small amounts of additive materials can be combined with any of the matrix resins used in this invention. For example, toughening agents such as polyurethanes or polyvinyl butyrals can be used or
10 pigments, fillers, ultraviolet absorbers, mold release agents, and the like, can be added.

It has been learned that ballistic performance is affected by the degree of adhesion between individual yarn filaments and the matrix resin. Ballistic
15 performance is believed to be improved when that adhesion is significant but low; and matrix resins have been identified and selected for use in this invention with that in mind. Epoxy resins are not recommended for use herein because it has been determined that adhesion
20 between the fibers and cured epoxy resins is so high that ballistic properties are adversely affected.

The composite of the present invention most clearly demonstrates its improved ballistic qualities by the use of yarns which, before embedment, have been coated
25 with an adhesion modifier. The preferred composite of this invention includes that coating and it is the use of that coating, in combination with the high tenacity, high elongation yarn, and the other elements of the composite, which defines the preferred form of this invention. The
30 function of the coating of adhesion modifier is to reduce the adhesion level between the p-aramid filaments and the resin matrix as discussed in greater detail below. When used, from about 0.2 to about 5 percent, by weight, of such adhesion modifier is applied to the yarns or fabrics
35 to achieve the desired ballistics results at areal densities of this invention. Less than about 0.2 percent of the modifier provides inadequate results and more than about 5 percent does not appear to provide significant additional improvement. While use of the adhesion modifier

yields a composite of improved ballistic performance, it should be noted that composites of improved performance are obtained when similarly treated yarns of the combination of high tenacity and high elongation to break
5 are used, whether or not the composite includes an adhesion modifier.

The adhesion modifier may be applied in any of a variety of ways to provide an even distribution on the surface of the filaments. For example, it may be
10 dissolved in a solvent, applied to the filaments and the solvent driven off, or it may be dispersed in a carrier (for example, water) and applied to the filaments, or it may be applied directly in the absence of other ingredients. One of the more common ways of application
15 is from a dispersion of the adhesion modifier in water.

The adhesion modifier may be characterized as a solid which is not readily absorbed or dissolved in the yarns or resin. As a solid, it will have less tendency to migrate during preparation of the composite or in use. It
20 is important that the modifier reduce the adhesion between fiber and matrix to limit shear loading on the fiber which is believed to prevent maximum utilization of ultimate fiber strength.

With the composites under consideration it has
25 been found that the desirable ballistic qualities are achieved at the low modifier add-on level specified, that is, from about 0.2 to 5 percent, by weight. At areal densities of about 0.4 to 6 pounds per square foot, the preferred level of modifier is from about 1 to 2 percent,
30 by weight.

Groups of adhesion modifiers for use with p-aramid yarns in this invention are certain fluorochemicals and paraffin waxes, and combinations thereof. The fluorochemicals may be described as 2-perfluoroalkylethyl
35 esters where the 2-perfluoroalkylethyl group has the structure $C_nF_{2n+1}(CH_2)_2-$ and $n=5-11$. Esters which are useful are those of methacrylic acid in polymeric form, citric acid urethane, and phosphoric acid or its ammonium salts, and the like. Esters of this type are shown, among

other places, in U.S. Patents 3,282,905 and 3,378,609.

The esters may be applied in combination with other polymers such as other acrylic, methacrylic and/or acrylamide polymers to promote pickup and dispersion of the fluorochemical on the p-aramid filaments and enhance durability. The paraffin waxes are solids derived from petroleum with melting points above room temperature. A paraffin wax with a melting point of about 60°C is generally preferred. The paraffin waxes may be applied with coupling agents such as a behenic acid ester derivative of melamine in order to promote the pickup and dispersion of the wax on the p-aramid filaments. A combination of fluorochemical and paraffin wax is the preferred surface modifier for practice of this invention.

15 Test Methods

Ballistic Limit

Ballistic tests of the composite samples were conducted in accordance with MIL-STD-662e as follows: A lay-up to be tested was placed in a mounting fixture designed to hold the sample perpendicular to the path of test projectiles. The projectiles were 17-grain fragment simulating projectiles (FSP) (MIL-P-46593A) and 2, 4, 16, and 64 grain right circular cylindrical (RCC) projectiles, except where indicated otherwise, and were propelled from a test barrel capable of firing the projectiles at different velocities. The first firing for each lay-up was for a projectile velocity estimated to be the likely ballistic limit (V_{50}). If the first firing yielded a complete penetration, the next firing was for a projectile velocity of about 50 feet per second less in order to obtain a partial penetration of the lay-up. On the other hand, if the first firing yielded no penetration or partial penetration, the next firing was for a velocity of about 50 feet per second more in order to obtain a complete penetration. After obtaining one partial and one complete projectile penetration, subsequent velocity increases or decreases of about 50 feet per second were used until enough firings were made to determine the ballistic limit (V_{50}) for that lay-up.

10

The ballistic limit (V_{50}) is calculated by finding the arithmetic mean of an equal number of the highest partial penetration impact velocities and the lowest complete penetration impact velocities, provided that there is not more than 125 feet per second between the highest and lowest individual impact velocities.

Areal density is defined as the weight per unit area of a rigid composite under test.

Tensile Properties

Tenacity is reported as breaking stress divided by linear density. Modulus is reported as the slope of the initial stress/strain curve converted to the same units as tenacity. Elongation is the percent increase in original length at break. Both tenacity and modulus are first computed in g/denier units which, when multiplied by 0.8826, yield dN/tex units. Each reported measurement is the average of 10 breaks.

Tensile properties for yarns are measured at 24°C and 55% relative humidity after conditioning under the test conditions for a minimum of 14 hours. Before testing, each yarn is twisted to a 1.1 twist multiplier (for example, nominal 1500 denier yarn is twisted about 2.1 turns/inch). Each twisted specimen has a test length of 25.4 cm and is elongated 50% per minute (based on the original unstretched length) using a typical recording stress/strain device.

The twist multiplier (TM) of a yarn is defined as:

$$TM = \frac{(\text{tpi}) (\text{Denier})^{1/2}}{73} = \frac{(\text{tpc}) (\text{dtex})^{1/2}}{30.3}$$

Wherein tpi = turns per inch and
tpc = turns per centimeter

35 Description of the Preferred Embodiments

EXAMPLE 1

This example includes manufacture and ballistic testing of flat ballistic composite panels of this invention and comparative ballistics testing of that

composite panel against panels made with similar materials and procedures but utilizing fabrics made from commercially available para-aramid yarns generally utilized for ballistics applications.

5 Yarns used in the fabric to make composites of the present invention had an average denier of 857 and an average tenacity/elongation/modulus of 26.5 gpd/4.23%/482 gpd. Yarn for the comparison fabrics was high strength poly(p-phenylene terephthalamide) having a denier of 840
10 and tenacity/elongation/modulus of 26.5 gpd/3.3%/750 gpd, sold by E. I. du Pont de Nemours and Company under the trademark designation Kevlar® 129.

Each of the yarns was woven into plain weave fabric having approximately 31 x 31 ends and picks per
15 inch (12.2 x 12.2 per centimeter). The fabrics were each open-width (jig) scoured to remove yarn finish and warp size and were then dried. The scoured and dried fabrics were immersed in a bath containing a dispersion of solid
20 adhesion modifier, passed through rollers to remove excess modifier material and dried and cured in an oven at about 360-370°F for 2-4 minutes. The fabrics were then rinsed with water and dried.

The adhesion modifier bath contained (1) a fluorochemical mixture, as a dispersion, comprising two
25 interpolymers and a surfactant. One interpolymers, constituting 1-2%, by weight, of the bath was derived from about 75% 2-perfluoroalkylethyl ester of methacrylic acid wherein the 2-perfluoroalkylethyl group had the formula $C_nF_{2n+1}(CH_2)_2-$, and n had a value from 5 to 11, and about
30 25% 2-ethylhexyl methacrylate. The second interpolymers, also, constituting 1-2% of the bath by weight was derived from about 97-98% of 2-ethylhexyl methacrylate, and 2% N-methylol acrylamide; (2) a wax/melamine mixture, as a
35 dispersion. The wax component, about 1.0-2.5% by weight of the bath, was a paraffin wax derived from petroleum with a melting point of about 60°C (140°F). The melamine component, constituting 1.0-2.5% of the bath was a melamine derivative wherein each non-ring nitrogen contained one methoxymethylene group and one

-CH₂-O-CO-C₂₁H₄₃ group. The ¹²dispersant for the wax mixture was a combination of the acetate salts of "Armeen" DM-18D and DM-14D sold by Armour Hess Chemicals Company; (3) about 0.2-0.4%, by weight of acetone as a wetting agent; and (4) about 91-95% water.

The fabric made from the high tenacity, high elongation yarn for use in this invention, had a dry basis weight of 6.87 oz/yd² and contained about 1.4% by weight of the adhesion modifier. This fabric was then impregnated (pregged) with a blend of 50% phenolic resin and 50% polyvinyl butyral by Westinghouse Electric Company. The resin was similar to that described in MIL-H-44099A, and was present in the amount of 15-18% by weight. The resin was uniformly applied to each side of the fabric and was partially cured by heating, reducing volatiles to 1-3% before composite fabrication.

To make the rigid composite of this invention, the pregged fabric was cut into rectangular pieces about 15" x 24"; 31 layers were stacked between polyester release films and 1/4" (6.4 mm) thick aluminum plates and were cured in a press at 200 psi (1379 kPa) and 330°F (166°C) for 60 minutes. The pressure was maintained until the press cooled to below 140°F (60°C), after which the samples were removed from the press. The top and bottom aluminum plates and release films were removed and the composites were cut into two 11" x 14" (27.9 cm x 35.6 cm) pieces for ballistic testing.

The fabric made from the commercially available ballistic yarn was, for comparison, scoured using the same procedure as the fabric of the invention and was treated similarly with the same adhesion modifier bath. The comparison fabric had a dry basis weight of 6.62-6.66 oz/yd² and contained about 1.35% of the adhesion modifier. This fabric was also pregged with the same 50/50 phenolic/polyvinylbutyral resin to the same resin level and similar rigid test panels were made using 32 layers of prepreg (instead of 31) to yield equivalent fiber content for comparison purposes.

13

Tables I and II, below, compare the ballistic performance for flat panels of the high tenacity, high elongation yarn of this invention with those of the comparison yarns showing the improvement in V₅₀ and energy

- 5 absorption capacity. For the 2-grain fragment, the composites of this invention averaged 9.6% higher V₅₀ and more than 20% higher energy absorption. For 16-grain right circular cylindrical fragments and 17-grain fragment
10 simulating projectiles, the improvement in V₅₀ was greater than 4% and the improvements in energy absorption was more than 8%. For all three ballistic threats, the differences are significant at greater than the 99% confidence level.

TABLE I - PANELS OF THIS INVENTION

15

	Fiber Areal Density	Composite Areal Density	%	V ₅₀ ft/sec.		
	<u>lb/ft²</u>	<u>lb/ft²</u>	<u>Resin</u>	<u>2gr</u> <u>RCC</u>	<u>16gr</u> <u>RCC</u>	<u>17gr</u> <u>FSP</u>
20	1.48	1.81	18.4	3989		
	1.48	1.81	18.4	4405		
	1.48	1.78	17.0	4062		
	1.48	1.78	17.0		2416	
25	1.48	1.78	17.1		2420	
	1.48	1.79	17.6			2257
	1.48	1.79	17.6			2238
30	Average V ₅₀ (ft/sec.)			4152	2418	2248
	Average Energy Absorp. (ft-lbs)			76.5	207	191
	Improvement over comparison, % V ₅₀ (from Table II)			9.6	4.1	3.9
35	Improvement over comparison, % Energy (from Table II)			20.1	8.4	8.2

14
TABLE II - PANELS OF COMPARISON MATERIALS

	Fiber Density ft/sec.	Areal Density lb/ft ²	Composite Density lb/ft ²	Areal % Resin	V ₅₀		
					2gr RCC	16gr RCC	17gr FSP
5	1.47	1.70	13.6	3646			
	1.47	1.74	15.4	3802			
10	1.48	1.79	17.4	3941			
	1.48	1.79	17.1	3940			
	1.46	1.76	17.0	3717			
	1.46	1.72	15.0	3770			
	1.46	1.72	15.0	3698			
15	1.47	1.72	14.6			2374	
	1.48	1.79	17.4			2283	
	1.46	1.75	16.6			2295	
	1.46	1.76	17.0			2343	
20	1.47	1.73	15.1				2141
	1.48	1.76	16.1				2191
	1.46	1.76	16.8				2144
	1.46	1.77	17.4				2176
25	Average V ₅₀ (ft/sec.)				3788	2324	2163
	Average Energy Absorp. (ft-lbs)				63.7	191	176

EXAMPLE 2

30 Helmets were made from impregnated samples of each of the fabrics of Example 1 by first cutting a series of pinwheel patterns as described in MIL-H 44099A Helmet-Ground Troops and Parachutists. A helmet preform was prepared by forming the pinwheels layer by layer and

35 tacking layers together with slight heat over a male headform according to the procedure described in MIL-H 44099A. The spokes of each pinwheel were overlapped along the sides of the helmet giving the equivalent of one extra layer every 5-6 pinwheels on the sides. To achieve a

40 uniform number of layers throughout, additional crown plies were located at the top of the helmet. Helmet preforms were made using each of the fabrics.

The helmets were molded at 300-330°F at 80-100 ton force in chrome plated matched tool-steel dies in the

45 size and shape of a medium size U.S. Army combat helmet. The mold surfaces were wiped with wax mold release prior to inserting the helmet shell preform into the hot dies. The mold was opened and closed several times during the

early portion of the molding cycle to allow volatiles to escape. The total molding time was 15 minutes. The helmet shell was removed from the mold while hot, allowed to cool and weighed.

5 Ballistic testing of the helmet shells was performed in accordance with MIL-H-44099A using 2, 4, 16, and 64 grain right circular cylindrical fragments commonly used in the U.S. Army to simulate fragmenting munitions. A V_{50} for each fragment used was determined as described
10 earlier.

For the helmets from the high tenacity, high elongation yarn of this invention, 29 die cut pinwheels plus four crown plies were used in each helmet shell, while for the slightly lighter fabric of the comparison
15 yarn, 31 pinwheels of slightly smaller size but identical shape were used with at least four crown plies. This gave an equal fiber content and areal density for comparison purposes.

Ballistic results are shown in Tables III and IV
20 from which it can be concluded that the V_{50} and energy absorption for helmets of this invention are significantly higher than for helmets made from the comparison fabrics.

TABLE III - HELMETS OF THIS INVENTION

	Nominal % Resin	Shell Wt. lbs.	<u>V₅₀ ft/sec.</u>			
			2 gr RCC	4 gr RCC	16 gr RCC	64 gr RCC
5	17	2.60	4400	3551		
	17	2.58	4121	3445		
	16	2.54	4444	3429		
10	16	2.53	4409	3405		
	17	2.59			2423	
	17	2.60			2439	
	16	2.43			2361	
15	16	2.54			2477	
	17	2.60				1894
	17	2.59				1709
	18	2.52				1849
20	<hr/>					
	Average V ₅₀ (ft/sec)		4344	3458	2425	1817
	Improvement over Comparison, % V ₅₀		5.28	6.01	2.41	0.89
	(From Table IV)					
25	Average Energy Absorp. (ft-lb.)		83.7	106	209	469
	Improvement over Comparison, % Energy		10.9	12.3	5.03	1.96
30	(From Table IV)					

TABLE IV - HELMETS OF COMPARISON MATERIALS

	Nominal % Resin	Shell Wt. lbs.	<u>V₅₀ ft/sec.</u>			
			2 gr RCC	4 gr RCC	16 gr RCC	64 gr RCC
35	17.3	2.55	4168	3285		
	17.3	2.50	3899	3132		
40	17.6	2.57	4186	3345		
	17.6	2.58	4250	3293		
	15	2.43	4127	3259		
	17.0	2.37			2372	
45	17.3	2.56			2394	
	17.3	2.49			2362	
	15.0	2.45			2339	
	15.0	2.43			2315	
	17.6	2.54			2428	
50	17.6	2.57				1784
	17.6	2.57				1818
55	<hr/>					
	Average V ₅₀ (ft/sec)		4126	3262	2368	1801
	Average Energy Absorp. (ft-lb)		75.5	94.4	199.	460.

Claims

1. A rigid composite comprising a resin matrix and a plurality of fabric layers made from p-aramid yarns exhibiting an elongation to break of greater than 4.0%, a modulus of less than 600 gpd, and a tenacity of greater than 23 gpd.
2. The composite of Claim 1 wherein the yarns comprise 50 to 90 % of the weight of the composite.
3. The composite of Claim 1 wherein the resin matrix is selected from the group consisting of polyester, phenolic, polyamide, and polyolefin.
4. The composite of Claim 1 wherein filaments of the p-aramid yarns are coated with from 0.2 to 5 percent, by weight, of a solid adhesion modifier.
5. The composite of Claim 4 wherein the solid adhesion modifier comprises 2-perfluoroalkylethyl ester.
6. The composite of Claim 4 wherein the solid adhesion modifier comprises paraffin wax.
7. The composite of Claim 4 wherein the solid adhesion modifier comprises a combination of 2-perfluoroalkylethyl ester and paraffin wax.
8. The composite of Claim 1 wherein there are additional layers of other materials included in the composite.
9. The composite of Claim 1 wherein the p-aramid is poly(p-phenylene terephthalamide).
10. The composite of Claim 1 wherein the fabric is woven.
11. The composite of Claim 10 wherein the woven fabric is a plain weave.
12. The composite of Claim 1 in the form of a helmet.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/04963

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 08 J 5/04, 5/06														
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="height: 40px; vertical-align: bottom;">IPC5</td> <td style="vertical-align: bottom;">C 08 J</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched⁸</div>			Classification System	Classification Symbols	IPC5	C 08 J								
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III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category *</th> <th style="border-bottom: 1px solid black;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 15%; border-bottom: 1px solid black;">Relevant to Claim No.¹³</th> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td style="vertical-align: top;">EP, A2, 0323541 (E.I. DU PONT DE NEMOURS AND COMPANY) 12 July 1989, see the whole document --</td> <td style="text-align: center; vertical-align: top;">1-12</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td style="vertical-align: top;">RESEARCH DISCLOSURE, vol. 30527, 1989, ANONYM: "Composite Helmets With Improved Ballistic Resistance ", see page 649 - page 650 --</td> <td style="text-align: center; vertical-align: top;">1-12</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td style="vertical-align: top;">US, A, 4560743 (FUJIWARA ET AL) 24 December 1985, see column 8, line 10 - line 22; claims 1,2 -- -----</td> <td style="text-align: center; vertical-align: top;">1-12</td> </tr> </table>			Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	Y	EP, A2, 0323541 (E.I. DU PONT DE NEMOURS AND COMPANY) 12 July 1989, see the whole document --	1-12	Y	RESEARCH DISCLOSURE, vol. 30527, 1989, ANONYM: "Composite Helmets With Improved Ballistic Resistance ", see page 649 - page 650 --	1-12	Y	US, A, 4560743 (FUJIWARA ET AL) 24 December 1985, see column 8, line 10 - line 22; claims 1,2 -- -----	1-12
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>														
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border-bottom: 1px solid black;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="border-bottom: 1px solid black;">28th September 1992</td> <td style="text-align: center; border-bottom: 1px solid black;">19 OCT 1992</td> </tr> <tr> <td style="border-bottom: 1px solid black;">International Searching Authority</td> <td style="border-bottom: 1px solid black;">Signature of Authorized Officer</td> </tr> <tr> <td style="text-align: center; border-bottom: 1px solid black;">EUROPEAN PATENT OFFICE</td> <td style="text-align: center; border-bottom: 1px solid black;">Sofia Nikolopoulou</td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	28th September 1992	19 OCT 1992	International Searching Authority	Signature of Authorized Officer	EUROPEAN PATENT OFFICE	Sofia Nikolopoulou				
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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/US 92/04963

SA 61816

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 28/08/92
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0323541	12/07/89	NONE	
US-A- 4560743	24/12/85	DE-A- 3467193	10/12/87
		EP-A-B- 0138011	24/04/85
		JP-A- 60052617	25/03/85

For more details about this annex : see Official Journal of the European patent Office, No. 12/82